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CONCERNING THE CUT-POINTS OF CONTINUOUS CURVES AND OF OTHER CLOSED AND CONNECTED POINT-SETS[1]

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The term "connected," as applied to point-sets, has been used by different authors with various meanings. In the present paper a point-set will be said to be *connected in the weak sense* (or, merely, connected[2]) if, no matter how it is divided into two mutually exclusive subsets, one of these subsets contains a limit point of the other one. The set M will be said to be *connected in the strong sense* if every two points of M lie together in some closed subset of M which is connected in the weak sense. The connected point-set M will be said to be *disconnected in the strong sense* (or, merely, *disconnected*) by a point-set K which is a proper subset of M provided $M-K$ is not connected in the weak sense. A point P belonging to a connected point-set M will be used to be a *cut-point in the strong sense* (or, merely, a *cut-point*) of M provided P *disconnects* M *in the strong sense.*

In a recent paper[3] Mazurkiewicz has shown (1) that every continuous curve contains at least two points neither of which disconnects it in the weak sense[4] and (2) that if M is a continuous curve which contains a simple closed curve k then k does not contain an uncountable set of points, each of which disconnects M in the weak sense.

These two theorems of Mazurkiewicz's will be called Theorems A and B, respectively. In a paper recently published I have shown that if a point disconnects a continuous curve in the weak sense then it also disconnects it in the strong sense. In the presence of this result Mazurkiewicz's Theorems A and B are equivalent to the theorems obtained from them by the substitution of the word "strong" in place of the word "weak." The resulting theorems will be called Theorems A' and B', respectively. Theorem A' is a special case of the following more general theorem.

Theorem A^*.—*Every closed, connected and bounded point-set whatsoever (whether it be a continuous curve or not) contains at least two points neither of which disconnects it in the strong sense.*

Theorem A^* is almost an immediate corollary of the following theorem which I proved in a paper[5] published in 1920.

THEOREM $A^\sharp$.—*If a closed, connected and bounded point-set M does not contain more than two points which are not cut-points of M then M is a simple continuous arc.*

The truth of Theorem A^* is a logical consequence of that of Theorem $A^\sharp$ and the fact that every simple continuous arc t contains two points (namely its end-points) which are not cut-points of t.

The following theorem includes Theorem B' as a special case but is much more general than Theorem B'.

THEOREM B^*.—*No closed and connected point-set M (whether it be a continuous curve or not) contains a closed and connected subset K (whether K be a simple closed curve or not) which contains an uncountable set of points each of which disconnects M but not K.*

Proof.—Suppose, on the contrary, that there exists a closed and connected point-set M which contains a closed and connected subset K containing an uncountable set T of points each of which is a cut-point of M but not of K. Then if X is any point of T, $M-X$ is the sum of two mutually exclusive point-sets neither of which contains a limit point of the other one. Since $K-X$ is connected, one of these point-sets contains $K-X$ and the other one does not. Let M_x denote the one which does not. Then if X_1 and X_2 are distinct points of T it is clear that M_{x_1} and M_{x_2} can have no point in common. By[6] the Zermelo postulate, there exists a set of points T° such that (a) for each point X in T there exists, in T°, just one point which belongs to M_x and (b) for each point Y in T° there exists, in T, just one point X such tht T_x contains Y. Since the set of points T° is uncountable it contains a point Z such that Z is a limit point of $T^\circ-Z$. But there exists in T a point W such that Z belongs to M_w. Since no point of $T^\circ-Z$ belongs to M_w, Z is not a limit point of $T^\circ-Z$. Thus the supposition that Theorem B^* is false has led to a contradiction.

THEOREM C.—*If M is a continuous curve which contains no simple closed curve and AXB is a simple continuous arc which lies wholly in M then every point of AXB (with the possible exception of its end-points A and B) is a cut-point of M.*

Proof.—Suppose, on the contrary, that there exists on AXB a point P distinct from A and from B and such that $M-P$ is connected. Then[7] A and B can be joined by a simple continuous arc AYB which is a subset of $M-P$. Let C denote the last point that the arc AYB has in common with the interval AP of AXB and let D denote the first point following C, in the order from A to B on AYB, that AYB has in common with the interval PB of the arc AXB. The interval CD of AXB forms, with the interval CD of AYB, a simple closed curve which is a subset of M. Thus the supposition that Theorem C is false leads to a contradiction.

THEOREM *D.—If the closed and connected point-set M is not a continuous curve then there exist two concentric circles K_1 and K_2 and a countable infinity of closed and connected point-sets M^1, M_1, M_2, M_3, . . . such that* (1) *each of these point-sets is a subset of M and contains at least one point on k_1 and at least one point on k_2, but contains no point without k_1 or within k_2,* (2) *no two of these point-sets have a point in common, and indeed, no one of them is a proper subset of any other connected subset of M which contains no point without k_1 or within k_2,* (3) *the set M^1 is the sequential limiting set of the sequence of sets $M_1, M_2, M_3, \ldots$.*

For indications of a proof of this theorem see my papers "Continuous sets that have no continuous sets of condensation"[8] and "A characterization of Jordan regions by properties having no reference to their boundaries."[9]

THEOREM *E.—In order that a closed, connected and bounded point-set M should be a continuous curve which contains no simple closed curve it is necessary and sufficient that every closed and connected subset of M should contain uncountably many points each of which disconnects M in the strong sense.*

Proof.—This condition is sufficient. For suppose, on the contrary, that there exists a closed, connected and bounded point-set M such that (1) M is not a continuous curve which contains no simple closed curve, and (2) every closed and connected subset of M contains uncountably many points each of which disconnects M in the strong sense. It follows, by Theorem B', that M is not a continuous curve. Hence there exist two circles k_1 and k_2 and a countable infinity of closed and connected point-sets M^1, $M_1, M_2, M_3, \ldots$ which satisfy, with respect to M, the conditions described in the statement of Theorem D. Suppose that M^1 contains an uncountable set of points T such that every point of T is a cut point of M. Then[10] if X is any point of T, $M - X$ is the sum of two point-sets neither of which contains a limit point of the other one. One of these point-sets (call it Kx) contains an infinite subsequence $M_{n_1}, M_{n_2}, M_{n_3}, \ldots$ of distinct point-sets belonging to the sequence $M_1, M_2, M_3, \ldots$. Let H_x denote the point-set $M - (K_x + X)$. For every point P belonging to $M^1 - X$ there exists a sequence of points $P_{n_1}, P_{n_2}, P_{n_3}, \ldots$ such that, for every m, P_{n_m} belongs to M_{n_m} and such that P is the sequential limit point of this sequence. Since $P_{n_1}, P_{n_2}, P_{n_3}, \ldots$ are all in K_x the point P must lie in K_x. Thus, for every point X belonging to T, the point-set K_x contains $M^1 - X$. Hence if Y is any point in $T - X$, the point-set K_y contains X and therefore H_y does not contain X. But $H_y + Y$ is clearly connected. Hence, since it contains one point, Y, in $K_{x\lambda}$, it must lie wholly in K_x. It follows that if X and Y are any two distinct points of T then $X + H_x$ and $Y + H_y$ have no point in common. Since, by hypothesis, there are uncountably many points in T_λ, it follows, by the Zermelo Postulate, that there exists an un-

countable set of points L such that (*a*) for each point X of T there is just one point in L belonging to H_x and (*b*) for each point Y of L there exists a point X in T such that Y belongs to H_x. Since L is uncountable it contains a point Z such that Z is a limit point of $L-Z$. But there exists in T a point W such that Z belongs to H_w. Moreover, no point of $L-Z$ is in the point-set $W + H_w$. Thus H_w contains a point Z which is a limit point of a set of points, $L - Z$, which lies wholly in K_w. Thus the supposition that $M^\dagger$ contains an uncountable set of cut-points of M has led to a contradiction. But the point-set $M^\dagger$ is a closed and connected subset of the point-set M. Thus the supposition that the condition of Theorem E is not sufficient has led to a contradiction.

The condition of Theorem E is also necessary. For suppose that M is a continuous curve which contains no simple closed curve. Then, by a theorem due to Mazurkiewicz,[11] if $M^\dagger$ is a closed and connected subset of M, $M^\dagger$ is itself a continuous curve. Hence $M^\dagger$ contains at least one simple continuous arc t. But, by Theorem C, every point of t (except possibly its end-points, is a cut-point of M. Thus $M^\dagger$ contains an uncountable set of points which are cut-points of M.

THEOREM *F.—In order that the continuous curve M should contain no simple closed curve it is necessary and sufficient that if K denotes the set of all those points of M that are not cut-points of M, then no subset of K disconnects M even in the weak sense.*

Proof.—This condition is sufficient. For suppose, on the contrary, that M contains a simple closed curve k, but no subset of K disconnects M. Let $K^\dagger$ denote the set $M - K$. Then clearly, every subset of M that contains $K^\dagger$ is connected. It follows that every point of M is a limit point of $K^\dagger$. Let A and B denote two distinct points of the simple closed curve k. By Mazurkiewicz's Theorem B, there exists on k a point C (distinct from A and from B) which does not belong to $K^\dagger$. Let k_A and k_B denote two circles with centers at A and B, respectively, and such that each of them lies entirely without the other one and neither of them contains or encloses the point C. Since M is connected im kleinen,[12] there exist, within k_A and k_B, respectively, two circles $k^\dagger{}_A$ and $k^\dagger{}_B$ such that every point of M that lies within $k^\dagger{}_A$ or $k^\dagger{}_B$ can be joined to A or to B, respectively, by a closed and connected of M that lies wholly within k_A or k_B, respectively. But, since every point of M is a limit point of $K^\dagger$ there exist two points $A^\dagger$ and $B^\dagger$ belonging to $K^\dagger$ and lying within $k^\dagger{}_A$ and $k^\dagger{}_B$, respectively. There accordingly exist two closed and connected point-sets M_A and M_B, both subsets of M, such that M_A contains A and $A^\dagger$ and lies wholly within k_A while M_B contains B and $B^\dagger$ and lies wholly within k_B. Since $K^\dagger$ is connected in the strong sense, it contains a closed and connected subset H which contains both $A^\dagger$ and $B^\dagger$. Let E and F, respectively, denote the first points which the intervals CA and CB of the arc BCA of the curve k

have in common with the closed point-set $H + M_A + M_B$. By a theorem of Janiszewski's,[13] the point-set $H + M_A + M_B$ contains a subset T which is irreducibly continuous from E to F. Let ECF denote that interval of the arc ACB which contains C and has E and F as its end-points. Consider the point-set $T + ECF$. If P is any point belonging to T and distinct from E and from F then, by a theorem of Janiszewski's,[13] either $T - P$ is connected or it is the sum of two connected point-sets T_E and T_F containing E and F, respectively. In either case $T + ECF - P$ is connected. Also if P is any point of ECF, distinct from E and from F, then $T + ECF - P$ is connected. Hence, by Theorem B^*, $T + ECF$ does not contain more than a countable number of points each of which disconnects M. But T contains uncountably many points of H and H is a subset of K^4. Thus the supposition that the condition of Theorem F is not sufficient has led to a contradiction.

The condition of Theorem F is also necessary. For suppose that M is a continuous curve which contains no simple closed curve. If C and D are two distinct point of M then M contains a simple continuous arc CD. By a theorem of Mazurkiewicz's[14] M contains a simple continuous arc AXB which contains CD but is not contained in any other simple continuous arc which is a subset of M. If P is a point belonging to the arc AXB but distinct from A and from B then by Theorem C, P disconnects M. Every point of M must be either an end-point of a maximal arc or a point (other than an end-point) of a maximal arc of M. Hence every point of M not an end-point of a maximal arc of M disconnects M. That an end-point of a maximal arc of M cannot disconnect M has been shown by Mazurkiewicz. Suppose now that K^* is a point-set every point of which is an end-point of some maximal arc of M and let C denote a point of AB distinct from A and from B. If P is any point of $M - K^*$ the point-set M contains a simple continuous arc PC. Clearly the arc PC cannot contain an end-point (except P in case P itself is such an end-point) of any maximal arc of M. Thus every point of $M - K^*$ can be joined to C by a simple continuous arc containing no point of K^*. It follows that $M - K^*$ is connected in the strong sense. Hence the condition of Theorem F is necessary.

[1] Presented to the American Mathematical Society, at Chicago, April, 1922.

[2] Cf. N. J. Lennes, "Curves in non-metrical analysis situs," *Amer. J. Math.*, **33**, 1911 (287–326).

[3] Mazurkiewicz, S., *Fundamenta Mathematicae*, **2**, 1921 (119).

[4] A sub-set K of a point-set M is said to *disconnect M in the weak sense* if $M-K$ is not connected in the strong sense.

[5] "Concerning simple continuous curves," *Trans. Am. Math. Soc.*, **21**, 1920 (333–347).

[6] Compare the argument from here on with that on page 338 of my paper "Concerning simple continuous curves," *loc. cit.*

[7] See my paper "Concerning continuous curves in the plane," *Math. Zeitschrift*, **15**, 1922(254–260).

[8] *Bull. Amer. Math. Soc.*, **25**, 1919 (174–176).

[9] These PROCEEDINGS, **4**, 1918 (364–370).

[10] Compare the argument from here on with that on pages 337–339 of my paper, "Concerning simple continuous curves," *loc. cit.*

[11] Mazurkiewicz, S., *loc. cit.*, p. 123.

[12] Cf. Hahn, H., *Wien. Ber.*, **123**, 1914 (2433).

[13] Janiszewski, S., "Sur les continus irreductibles entre deux points," *J. l'Ecole Polytech.* **16**, 1911–1912 (79–170).

[14] Mazurkiewicz, S., *loc. cit.*, p. 129.

THE REDUCTION DIVISION IN HAPLOID, DIPLOID, TRIPLOID AND TETRAPLOID DATURAS

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It is probable that the number and nature of the chromosomes which the zygotic cell of a flowering plant has received from the sperm nucleus and the egg-cell will account for most of the inherited qualities of the resulting plant. Hence an important time in the life history of such a plant is the brief period when the parental contributions to the gametes are being distributed. This period comprises the first division in the mother-cells of the pollen.

In the ordinary diploid Datura, there are visible, at late prophase and metaphase of the first division, 12 pairs of chromosomes, among which at least 6 sizes may be made out.[2] Usually, the two chromosomes of a pair are joined at both ends (diagram 1, middle of second column); but not uncommonly they are connected at one end only,[7] and rarely they are separate. The two members of each pair are, of course, of the same size; the formula for the bivalents being $L_2 + 4l_2 + 3M_2 + 2m_2 + S_2 + s_2$. In the haploid Datura[3] (diagram 1, first column) which has only one group of 12 chromosomes, the chromosomes are usually straight, and single, not in pairs; the size formula being $L + 4l + 3M + 2m + S + s$. In the triploid plants there are 36 chromosomes,[6,9] which form 12 sets of three connected chromosomes each,[8,2] the formula for the trivalents being $L_3 + 4l_3 + 3M_3 + 2m_3 + S_3 + s_3$. Usually there is one pair of chromosomes joined at both ends, as in the diploid plants, with the third chromosome attached by one end to one of the junctions (diagram 1, middle of column 3). Not uncommonly, however, there is a Y-shaped arrangement of the chromosomes, or the 3 chromosomes are joined end to end to form a usually hook-shaped rod. (The two forms at the bottom of column 3 are rare.) Occasionally one (or

more) of the single chromosomes or chromosome pairs remains isolated, which is also a not infrequent occurrence in triploid Cannas.[1] In the true tetraploid Daturas, before the first division in the microspore mother-cells, the 48 chromosomes are in 12 sets with 4 connected chromosomes in each,[5] the formula for the quadrivalents being, $L_4 + 4l_4 + 3M_4 + 2m_4 + S_4 + s_4$. (Sometimes one or more pairs, or single chromosomes, remain unconnected.) A common arrangement is that of two pairs, the members of which are connected at both ends, and the pairs secondarily joined at one of these connections, the planes being sometimes at right angles (diagram 1, center of column 4). The two pairs are also often folded to-

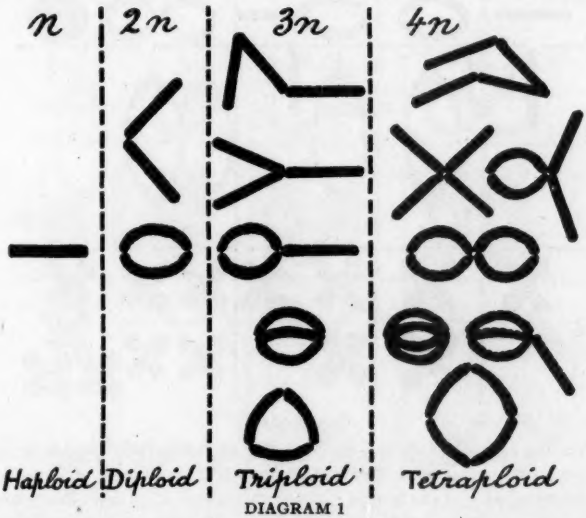

DIAGRAM 1

Arrangement of the chromosomes at the late prophase and early metaphase of the first division in the pollen-mother-cells of Datura Stramonium. (*Column 1*)—Straight chromosome of the haploid plant. (*Column 2*)—In the center, the ordinary pair of two bent chromosomes. Above, the V-shaped arrangement. (*Column 3*)—In the center, the ordinary form of a ring with an attached rod. Above, the less common Y-shaped arrangement, and the not uncommon hooked form. Below are two rare combinations. (*Column 4*)—In the center, the double ring, or figure of 8, the rings of which are often in different planes. Below this, to the left, the combined rings. The other forms are not so common.

gether so as to form a double hoop (diagram 1, column 4, below and to the left of the middle). The other forms are not so conspicuous or not so common.

In the first division in the pollen-mother-cells of the haploid plant, each chromosome moves, apparently by chance, in one or the other direction; so that two groups of 6 + 6, 5 + 7, 4 + 8, etc., are usually formed. After

the second division, the resulting nuclei may have 1, 2, 3, 4, 5, etc., chromosomes each. When the cytoplasm has divided, microcytes,[2] or small microspores with deficient numbers of chromosomes, are formed. These diminutive pollen-grains with less than 12 chromosomes apparently lose their cytoplasm and perish.[3] In the diploid Datura, the two chromosomes of each pair pull apart in the usual manner, remaining for some time connected by their ends (diagram 2, column 2). When they have separated

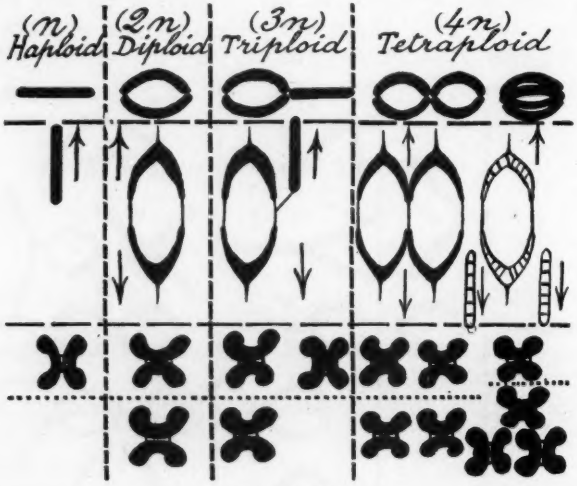

DIAGRAM 2

Arrangement of the chromosomes in the pollen-mother-cells of Datura Stramonium; *line 1*, at the late first prophase; *line 2*, at the late first metaphase or early anaphase; *line 3*, at the metaphase of the second division. (*Column 1*)—Each chromosome of the haploid plant moves in one or the other direction. It splits longitudinally before the second metaphase, the halves being shaped like bent dumb-bells, and the whole forming a pseudo-tetrad, of which there are 1 to 11 in the second-metaphase groups. (*Column 2*)—The chromosomes of each pair in diploid plants move in opposite directions, with about one exception in 2000 cases. They thus form second-metaphase groups of 12 split chromosomes each. (*Column 3*)—The two paired chromosomes of the ordinary trivalent separate regularly, and the odd chromosome goes in either direction, forming second-metaphase groups with from 12 to 24 chromosomes each. (*Column 4*)—The two pairs which usually compose a quadrivalent often separate regularly, giving two chromosomes to each pole. But in about one quadrivalent in 36, the chromosomes probably separate as 3 to 1. Thus, less than three-quarters of the second metaphase groups have 24 chromosomes.

the longitudinal split for the second division becomes obvious. Nondisjunction is normally rare, one case (comprising 3 adjacent cells) having been noted in 500 pollen-mother-cells at normal temperatures. In the pollen-mother-cells of triploid Daturas, the two paired chromosomes of each

set usually move towards opposite poles as in diploid plants; and the third chromosome, which was laterally connected, moves to either pole, as in the haploid Daturas. The resulting distribution has been shown[2] to be closely comformable to the laws of chance. Whether non-disjunction is present or not in the triploid plant cannot be told from the chromosome distribution. In the true tetraploid Daturas, two chromosomes, out of the double pair forming a figure of 8, have been seen passing towards one pole, and the other two towards the other pole (diagram 2, column 4). But in one quarter and more of the pollen-mother-cells this regular distribution does not occur with regard to all of the 12 quadrivalents. In one (or more),

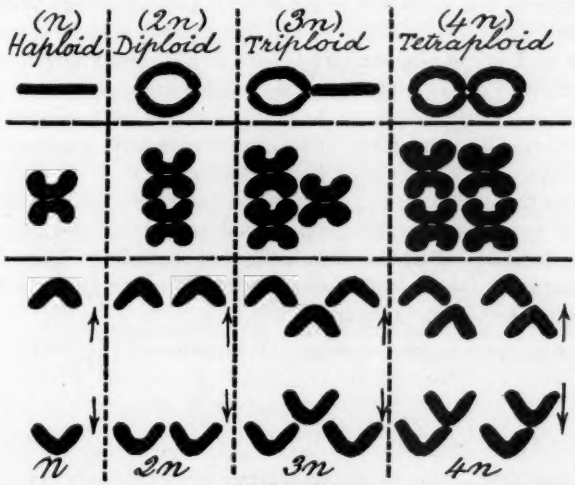

DIAGRAM 3

The results of non-reduction in the pollen-mother-cells of Datura Stramonium. (*Column 1*)—The 12 chromosomes of the haploid plant divide longitudinally, forming pseudo-tetrads. These separate, as at the second metaphase, forming two pollen-grains with 12 chromosomes each. (*Column 2*)—The 12 bivalents apparently form two pseudo-tetrads each. These divide, as in the second anaphase, giving rise to two pollen-grains with 24 chromosomes each. (*Column 3*)—Two pollen-grains result, with 36 chromosomes each. (*Column 4*)—Two pollen-grains are formed from each pollen-mother-cell, having 48 chromosomes each.

quadrivalents in such cases of non-disjunction, three chromosomes go to one pole, and one to the other pole. This is known by the results of the division, which give 23 + 25 (or 22 + 26, etc.) chromosomes, instead of 24 + 24, in more than one quarter of the cells. This non-disjunction would occur for the individual quadrivalents, by calculation, in slightly less than three per cent of the possible cases. (The figure in outline in diagram 2, column 4, serves merely to indicate the result, the details being

as yet unobserved.) The lower part of column 4, diagram 2, shows the longitudinally split chromosomes prepared for the second division; the total numbers in the mother-cell being on the one hand 24 + 24, and on the other hand either 23 + 25, 22 + 26, 21 + 27, or in one case, 20 + 28.

In non-reduction, the chromosomes at the metaphase, instead of having a reduction division, divide longitudinally, and the two halves separate as in the normal second division, the first (reducing) division being omitted. This frequently occurred in the haploid Daturas examined, and the resulting pollen-grains, with 12 chromosomes each, appeared to constitute the full-sized and unaborted pollen-grains of the haploid plant.[3] In normal diploid Daturas, non-reduction, so far as yet noted, is rare, except after cold; double-sized pollen-grains being formed, presumably with 24 chromosomes each. In triploids, non-reduction has been seen[2] to occur fairly frequently, and the resulting pollen-grains have 36 chromosomes. In true tetraploids, non-reduction is rare, but a 48 + 48 division has been observed in the pollen-mother-cells; and giant pollen-grains of double volume, containing presumably 48 chromosomes, have been seen.

Pollen-mother-cells (microsporocytes) at the reduction division have a volume of cytoplasm, nearly proportional to the number of complete haploid groups of chromosomes which they contain.[4] The following measurements of Datura pollen-mother-cells, between the late first prophase and the second metaphase, show this.

Kind of plant	Number of pollen-mother-cells	Diameters found	Diameters calculated
Haploid.....	100	1.00	1.00
Diploid.....	100	1.32	1.26
Triploid.....	40	1.43	1.44
Tetraploid.....	100	1.69	1.59

The fourth column gives the cube roots of 1, 2, 3, and 4. The diameter of the mother-cells in the tetraploid plant is about 6 per cent above the calculated figure.

Summary.—(1) The homologous chromosomes at the late prophase and the metaphase of the first division in the pollen-mother-cells of diploid, triploid, and tetraploid Daturas are connected by their ends.

(2) No chromosomes are connected in the haploid Datura.

(3) There are, as usual, 12 pairs of connected chromosomes in the diploid plant, the connection occurring usually at both ends.

(4) There are 12 trivalents in the triploid plant, there being usually two chromosomes connected at both ends, and one laterally attached, with one free end.

(5) There are 12 quadrivalents in the tetraploid plant; the usual arrangement being two pairs, the component chromosomes of which are joined at both ends, and the pairs connected with one another at one or both junctions.

(6) Non-disjunction, under ordinary conditions, is rare in the diploid, but of regular occurrence in the tetraploid plant, in which it happens in more than one quarter of the pollen-mother-cells.

(7) Non-reduction, at normal temperatures, is rare in the diploid, triploid, and tetraploid, but apparently of regular occurrence in the haploid plants. In this way pollen-grains with the somatic numbers of chromosomes are produced.

(8) The volume of the cytoplasm in the pollen-mother-cells, at the reduction division, is closely proportional to the number of haploid groups of chromosomes present in the cell.

[1] Belling, J., 1921, "The Behavior of Homologous Chromosomes in a Triploid Canna," these PROCEEDINGS, **7**, 197–201.

[2] Belling, J., and A. F. Blakeslee, 1922, "The Assortment of Chromosomes in Triploid Daturas," *Am. Nat.*, **56**, 339–346.

[3] Blakeslee, A. F., J. Belling, M. E. Farnham, and A. D. Bergner, 1922, "A Haploid Mutant in .... Datura Stramonium," *Science*, **55**, 646–647.

[4] Marchal, El., et Em., 1909, "Aposporie et Sexualité chez les Mousses," *Bul. Acad. Roy. Belgique* (Classe des Sciences), **9–10**, 750–778.

[5] Marchal, El. et Em., 1911, "Aposporie et Sexualité chez les Mousses," *Ibid.*, **12**, 1249–1288.

[6] de Mol, W. E., 1921, "Over het voorkomen van heteroploide varieteiten van Hyacinthus orientalis L., in de Hollandshe kulturen." *Genetica*, **3**, 97–192.

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[8] Osawa, I., 1920, "Cytological and Experimental Studies in Morus, with Special Reference to Triploid Mutants," *Bul. Imp. Sericult. Exp. Sta. Japan*, **1**, 317–369.

[9] van Overeem, C., 1922, "Über Formen mit abweichenden Chromosomenzahl bei Oenothera," *Beih. z. Bot. Centralbl.*, **B39**, Abt. 1, Heft 1, S. 1–80.

THE VARIATION AND INHERITANCE OF MILK CHARACTERS

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Communicated, March 7, 1923

In 1919 the writer spent a year as a guest of Count F. Ahlefeldt-Laurvig at Tranekjaer Castle, Denmark. He had there the opportunity to study daily the remarkable herd of dairy cattle on the manor. The 700 cows are managed and fed uniformly and on a strictly commercial basis. The composition of the herd is unique. It contained originally two breeds, Red Danish dairy cattle and Jersey Cattle. Twenty years ago, Count Ahlefeldt proposed to the Experiment Station of the Royal Veterinary and Agricultural College at Copenhagen to use his herd for a series of experiments to investigate through an extensive control of feeding, growth,

amount of milk, fat-content of the milk, duration of life, and expense for milking, care, interest and amortisation, etc. which of the breeds (including crossbreds) commercially was the most profitable. Fourteen yearly reports have been published by the station, but no attempt had been made to utilize the huge material for genetic research. In 1921, Count Ahlefeldt entrusted me with all the original records and these were brought to America. Their study was begun at the University of Illinois, and completed at the Bussey Institution of Harvard University.

1. *The Cycle of Milk Secretion and Its Component Parts.*—We can call the series of occurrences in the functioning of the milk glands from birth to birth, the cycle of milk secretion. It can be subdivided in two ways, according to the activity of the milk organs or to the condition of pregnancy. From the first point of view, the cycle consists of the lactation period and the dry period, from the second of the non-pregnant and the pregnant or gestation period. Using the first lactation period records for the two pure breeds, we get the values for the usual statistical constants given in table I.

TABLE I

		RED DANISH	JERSEY
Cycle of milk secretion.....	Mean	54.69±0.37 weeks	53.96±0.50 weeks
	S.D.	7.77±0.27 weeks	7.40±0.35 weeks
Lactation period.....	Mean	46.43±0.35 weeks	46.55±0.51 weeks
	S.D.	7.52±0.24 weeks	7.59±0.35 weeks
Dry period.....	Mean	7.26±0.08 weeks	7.40±0.13 weeks
	S.D.	1.76±0.06 weeks	2.02±0.09 weeks
Non-pregnant period.....	Mean	14.68±0.35 weeks	14.03±0.51 weeks
	S.D.	7.58±0.25 weeks	7.64±0.36 weeks
Gestation period.....	Mean	277.80±0.31 days	278.13±0.42 days
	S.D.	6.33±0.22 days	6.19±0.30 days

There is no correlation in the Red Danish breed between the length of the lactation period and the length of the dry period, but in the Jersey breed a negative correlation of -0.25 exists.

2. *Variation in the Quality of Milk Secretion.*—It is a familiar fact, that there is a very considerable variation in the amount of milk produced by different cows, and by the same cow at different times. These differences, which are of great economic importance, are brought about by a multitude of causes. These are partly obvious, partly more or less obscure. A separation of variations due to inheritance from those due to environmental conditions is desirable, but by no means an easy matter, especially in the case of quantitative characters. In order to approach a demonstration of the differences in the genetic constitution of a number of individuals with respect to a certain character, it is necessary to eliminate as many other causes of variation as possible. An extensive study of factors influencing the amount of milk secreted is therefore of prime importance.

It is obvious that, other things being equal, the longer the lactation period, the greater the total yield. We propose therefore to consider the question, what factors determine the variation in length of lactation period demonstrated in table 1. The average lactation curve is well known, it ascends rapidly through 3–4 weeks to a maximum from which there is an almost straight decline. As possible causes influencing the length of lactation period several suggest themselves. A cow starting off with a high production might keep on milking longer than another with a small initial yield. The cow with a rapid falling off of the milk might stop milking earlier than one with a gradually declining yield. Finally the time of successful breeding, which determines the birth time of the next calf, enters as a potential cause of variation. The first of these possible causes of variation has been shown in the present study to be of no importance, the correlation between maximum yield and length of the lactation period being zero. As a measure of the slope of the milk curve has been used the ratio between gross production in the second and in the first 10-week sections of the lactation period. This measure of slope is really a measure of maintenance ability. There is a significant difference between the two breeds, the ratio of the Jerseys being 5% lower than for the Danish, meaning that the Jerseys have less ability to maintain the initial production. As there has been shown to be a negative correlation between initial yield and the ratio, the difference between the breeds, of which the Danish is the higher milking, is still more striking. The correlation between the slope ratio and length of lactation period is for the Danish breed $+0.168 \pm 0.045$, for Jerseys $+0.045 \pm 0.067$. The first is possibly significant, but at the most, slope is a negligible factor in determining the length of the lactation period. Finally time of successful breeding (interval between birth and breeding) has been correlated with the length of lactation period. The coefficients are for the Danish $+0.943 \pm 0.005$, for the Jerseys $+0.891 \pm 0.014$. These show a very high degree of agreement between the two variables. The degree of determination in the variation of length of lactation period by variation in breeding time is between 80 and 90%.

The amount of milk (in kg.) secreted in the first lactation period during each of the first four 10-week sections (the first including the 2nd to the 11th week, etc.) is given in table 2.

TABLE II

SECTION		RED DANISH	JERSEY
1	Mean	790.35±7.04 kg.	638.94±8.68 kg.
	S.D.	153.02±4.98 kg.	131.10±5.46 kg.
	Coeff. of var.	19.38±0.63	20.52±0.95
2	Mean	677.56±6.19 kg.	502.88±7.27 kg.
	S.D.	134.44±4.37 kg.	109.83±5.12 kg.
	Coeff. of var.	19.84±0.64	21.83±1.01
	Mean	555.93±5.77 kg.	409.62±6.24 kg.

TABLE II (*Continued*)

SECTION		RED DANISH	JERSEY
3	S.D.	125.50±4.09 kg.	94.33±4.40 kg.
	Coeff. of var.	22.57±0.73	23.00±1.07
	Mean	382.91±6.44 kg.	277.40±7.16 kg.
4	S.D.	139.89±4.55 kg.	108.17±4.37 kg.
	Coeff. of var.	36.53±1.28	39.02±1.80

Of importance is the increase in the coefficient of variation, indicating that new causes of variation appear during the lactation period or that a cause of increasing importance influences the amount of milk. It is natural to seek the cause of increased variation in the time of breeding. We have therefore correlated time of breeding with the amount of milk secreted in each of the four 10-week sections and obtained the values for the correlation coefficients given in table 3.

TABLE III

SECTION	RED DANISH	JERSEY
1	0.072±0.046	0.086±0.066
2	0.124±0.045	0.155±0.065
3	0.234±0.044	0.253±0.062
4	0.551±0.032	0.553±0.046

These are important because they show that a factor, that has probably nothing to do with the cow's milk secreting ability, enters as a very important factor in determining the total amount of milk the cow will yield. In the first 10-week section this factor is of no importance, of very little in the second, but enters as a very considerable determining factor in the later sections. As the milk yield in the first and in smaller degree in the second 10-week section is to a greater extent determined by innate factors, they are obviously a better measure of a cow's milk yielding ability than the records covering a longer period.

There are a number of causes of variation which make the direct comparison of the records of different cows difficult and fallacious.

Almost all cows in the present material have been calving during the six winter months. The time of calving influences very materially the amount of milk produced, the difference between the averages for October and March calvers amounting to 16%. A correction is therefore necessary and all records are brought to a March basis.

The influence of the age of the heifer at the first calving affects the production during the first lactation period. This effect is largely reduced by separating the cows into two groups, cows 24 to 27 months old and 28 to 35 months old at calving.

Finally the yield of the same cow in successive periods varies displaying a certain well known regularity. There is anyhow a high degree of correlation between the yield in different periods.

Taking every pro and contra in consideration, it is the conviction of the writer that the first 10-week section of the first lactation period best displays the genetic variations and therefore at present is the most reliable measure of a cow's milk yielding ability, though not an ideal one.

3. *Variation in Milk Production in Crossbreeding Experiments.*—The present material includes besides the two parental pure breeds, halfbreds, $^3/_4$ Danish, $^3/_4$ Jerseys and $^7/_8$ Jerseys. No F_2 has been raised. The records have been treated extensively and the actual as well as the corrected data have been used. Table 4 is only an example of the results.

TABLE 4

CORRECTED MILK PRODUCTION IN FIRST 10-WEEK SECTION OF FIRST LACTATION PERIOD, COWS 28–35 MONTHS OLD

	MEAN	S. D.	COEFF. OF VAR.
Red Danish	895.7±11.3 kg.	149.5± 8.1 kg.	16.7±0.9
Jersey	711.5±13.8 kg.	148.5±10.0 kg.	20.9±1.3
Crossbred	832.4±18.6 kg.	156.5±12.8 kg.	18.8±1.6
$^3/_4$ Danish	880.6±36.9 kg.	160.5±27.6 kg.	18.2±3.0
$^3/_4$ Jersey	742.3±18.6 kg.	137.0±13.1 kg.	17.1±1.6
$^7/_8$ Jersey	700.0±23.4 kg.	108.0±16.6 kg.	15.4±2.3

4. *Variation in Butterfat Percentage.*—It is a well known fact that the average fat percentage of the milk in different breeds is very different. The present material displays another striking breed difference. The change in fat percentage with progressing lactation follows in the Jersey material practically a straight line, beginning at about 4.6% and reaching after 42 weeks 6.1%. The Danish cows begin at 4.1%, then follows a gradual decline during the first 2 months, the lowest percentage being 3.4%. After this minimum the fat percentage gradually increases, following the course of a straight line, till it reaches its first high value.

As probably the best and most reliable measure of fat percentage, has been chosen the average percentage during the first 10-week section of the first lactation period.

TABLE 5

	MEAN	S. D.	COEFF. OF VAR.
Red Danish	3.56±0.01%	0.33±0.01%	9.27±0.29
Jersey	4.94±0.03%	0.51±0.02%	10.32±0.42
Crossbred	4.21±0.03%	0.45±0.02%	10.69±0.59
$^3/_4$ Danish	4.04±0.05%	0.35±0.04%	8.66±0.92
$^3/_4$ Jersey	4.53±0.04%	0.46±0.03%	10.15±0.57
$^7/_8$ Jersey	4.60±0.06%	0.42±0.04%	9.13±0.89

The relationship between amount of milk and percentage of fat is a much discussed problem. The Red Danish material shows, that these two variables are quite independent, while the Jersey material, where the problem has been approached by different methods including partial correlation, consistently gives a coefficient of -0.33.

The influence of age is negligible and the influence of season is not so great as to warrant any special precautions.

5. *Variation in Fat Percentage in Crossbreeding Experiments.*—The fat percentage in first 10-week section of the first lactation period for the different genetic groups is given in table 5 as an example of the studies relating to this problem.

The shape of the lactation curve for the Crossbreds is intermediate between the shapes displayed by the parental breeds. Of interest is further the coefficient of correlation between milk amount and fat percentage in the different genetic groups as given in table 6.

TABLE 6

Red Danish	$+0.055 \pm 0.044$	$^3/_4$ Danish	-0.011 ± 0.148
Jersey	-0.332 ± 0.051	$^3/_4$ Jersey	-0.149 ± 0.078
Crossbred	-0.246 ± 0.073	$^7/_8$ Jersey	-0.282 ± 0.134

6. *The Variation in Butter-Fat Production.*—The variation here dealt with is determined partly by the amount of milk, partly by the percentage of fat. From the Red Danish material it has been found that 75% of the variation is due to variation in milk amount, 25% to the variation in fat percentage. The former is thus of most importance.

The influence of season is of considerable importance, cows calving in October–December producing about 15% less butter-fat than those calving in January–March. By adding 15% to the former, the two groups are brought approximately to the same basis.

7. *The Variation in Butter-Fat Production in Crossbreeding Experiments.*—Table 7 gives as an example the corrected production of butter-fat in first 10-week section of first lactation period for cows 28–35 months old at calving.

TABLE 7

Red Danish	32.12 ± 0.57 kg.	$^3/_4$ Danish	34.00 ± 1.85 kg.
Jersey	36.54 ± 0.99 kg.	$^3/_4$ Jersey	36.16 ± 0.88 kg.
Crossbred	35.72 ± 0.78 kg.	$^7/_8$ Jersey	31.55 ± 1.08 kg.

8. *The Mode of Inheritance of Milk Characters.*—There is no doubt that the mode of inheritance of milk characters falls in that group of inheritance phenomena to which the term blending has been assigned. The treatment of the material fails to disclose the action of any single Mendelian factor. There is no significant difference in the variability of the different genetic groups. The heterozygosity of the parental breeds and the probable complexity of the characters fully account for this. An F_2 generation might have given valuable results but unfortunately has not been reared.

THE SIGNIFICANCE OF THE EXPERIMENTALLY DETERMINED CRYSTAL STRUCTURES OF THE ALKALI POLYHALIDES

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By means of a new and powerful method of X-ray analysis the crystal structures of some of the alkali polyhalides have just been determined by the writer in association with Professor William Duane. Both the details of the method and of the analyses have been presented in other notes.[2] It is the purpose of this note to bring the new experimental data to bear upon the great uncertainty concerning the real constitution of these unique compounds which has prevailed since their discovery 30 years ago by Wells and Wheeler.[3]

Few experimental facts concerning the alkali polyhalides have been known up to the present time, except that solutions of cesium iodide, for example, are able to dissolve iodine, or bromine or chlorine, and produce crystals whose chemical analyses may be expressed by the empirical formulas CsI_3, CsI_5, $CsIBr_2$, $CsBrI_2$, $CsICl_2$, CsIBrCl, etc. Wells and Penfield[4] found that the trihalides crystallize similarly and may even be isomorphous. Stability measurements by the writer and by Ephraim[5] show that the trihalides form a remarkable continuous series, in which maximum dimensions of the atoms are favorable to stability: thus CsI_3 is most stable, while $CsCl_3$, KBr_3 or NaI_3 do not exist; and KI_3, $RbBrI_2$ and $CsBr_3$ are all equally stable. These measurements also indicate very clearly that all salts which contain iodine form one stability and crystallographic series, and those containing bromine in the absence of iodine another; in other words, the heaviest halogen atom has a defining influence, so that such a formula as $CsBrI_2$ might more properly be written CsI.BrI.

It has been suggested that in the alkali polyhalides the metal may have a higher primary valence, as is true of gold (which is in the same periodic group as the alkali metals) in the known reaction $Au^+Cl + Cl_2 = Au^{+++}Cl_3$. Again, it has been advocated by Remsen,[6] Wells and Penfield,[4] McCombe and Reade[7] (in February, 1923), and others, that one or more of the halogen atoms have a higher valence than is true in the simple halides. Several experimental facts disprove these contentions. Freezing point and conductivity experiments show that the ions in a solution of CsI_3, for example, are Cs^+ and I_3^-. This means that in a molecule of the trihalide the single primary valence bond which holds cesium and iodine together in CsI is unchanged, but that the iodide ion is able to associate with itself two additional atoms of iodine, or a halogen *molecule* capable of independent existence, and form complexes. In solution the equilibrium $I^- + I_2 \rightleftarrows I.I_2^-$

is very definitely established. Besides the complex anions of the halogens, those of sulfur, $S.S^{--}$, S_2S^{--}, S_3S^{--}, S_4S^{--} and S_5S^{--}, have been identified by Küster,[8] and those of tellurium, $TeTe^{--}$ and Te_3Te^{--} in the beautiful work of Kraus.[9] These are all manifestations of secondary valence just as truly as the combinations of water with salts to form hydrates or of ammonia to form ammines (cationic complexes) are secondary valence phenomena. These experiments, however, cannot explain the structure and the real nature of these complex groups, and they cannot be interpreted so as to give concrete knowledge of secondary valence. The actual crystal structures give this information unmistakably, and in addition answer many questions which are confronting chemists, such as whether or not the identity of the single chemical molecule is retained in the space lattice of a solid.

The crystal structures of four alkali polyhalides have now been more or less completely determined. The results are as follows:

KI_3 monoclinic $d_{100} = 4.70 \times 10^{-8}$ cm.

CsI_3 orthorhombic $d_{100} = 4.49, d_{010} = 6.43, d_{001} = 7.02 \times 10^{-8}$ cm.

$CsIBr_2$ orthorhombic $d_{100} = 4.26, d_{010} = 5.91, d_{001} = 6.90 \times 10^{-8}$ cm.

$CsICl_2$ rhombohedral hexagonal d (Cs to I along trigonal axis) $= 6.102 \times 10^{-8}$ cm.

Of these the first three have been studied by the writer[2] and the last by Wyckoff.[10] In spite of the fact that three crystallographic systems are represented, the exceedingly interesting result comes out that all four crystal structures present precisely the *same* relative arrangement of atoms in the unit parallelopipeda, if these unit cells are properly oriented so as to include one molecule. It is of secondary importance for the purpose in hand that the unit cell planes may be perpendicular or inclined to each other, or that the axes may be equal or unequal in length. This arrangement is as follows: metal atoms at the corners of the cell, and halogen atoms inside the cell *in a line* on the body diagonal, with the heaviest halogen atom at the center and the other two on the diagonal on either side equidistant from the center (if they are alike). In CsI_3 and $CsIBr_2$ the distance from the center along the diagonal of the two iodine or two bromine atoms is half that from the center to the corner; hence the coördinates are $(a/4, b/4, c/4)$ and $(-a/4, -b/4, -c/4)$, where a, b, and c are the edge lengths of the unit cell in three directions at right angles. In $CsICl_2$ the chlorine atoms have a parameter of .19 of the total length of the diagonal on either side of the central iodine atom, so that the unit cell is a rhombohedron instead of a rectangular parallelopiped. It is an interesting conjecture whether the orthorhombic variety of $CsICl_2$, if it does exist, is produced by a displacement of the chlorine atoms farther along the diagonal from the center. The only other possibility would be that a chlorine atom occupies a central position instead of the iodine, but this should be very

much less stable than the other arrangement. There is no doubt but that the normal tendency of the compound is to form the rhombohedral hexagonal form.

In KI_3 the unit cell is a monoclinic prism which has been formed by the slight deformation of a cube. The parameter of the two non-central iodine atoms on the body diagonal is slightly less than .25 (approximately .23) of the total length of the diagonal.

Thus in every case experimentally observed the three halogen atoms are closely associated together in a line, and constitute a singly acting group in the space lattice just as truly as they do in the formation of complex anions in solution, and just as truly as the identity of the complex cation $[Ni(NH)_6]^{++}$ is perfectly maintained in the space lattice of crystals, as proven by the crystal structures of nickel halide and nitrate hexammoniates determined by Wyckoff.[11] There is every reason to believe that the facts discovered for the four typical polyhalides are also true of all other polyhalides, since they are so closely related crystallographically and chemically. At least it is practically certain that the relative arrangement of atoms in the unit cells is the same. The experimental proof that the heaviest halogen atom is central in the halogen group is entirely compatible with the facts also experimentally observed that salts containing iodine form one stability and crystallographic series and bromine another. Differences in the polyhalides therefore arise only in the size and shape of the crystal unit cell, and in most cases even the latter is the same.

While it is clear that the secondary valence group of the polyhalides, as well as those of ammines and hydrates, maintains its individuality in the crystal space lattice, it is still a question whether the whole molecule of KI_3, for example, exists as such in the space lattice. It has been clearly demonstrated that the simple chemical molecule Na-Cl as it is found in vapor does not exist as such in the crystal lattice, since every sodium atom is surrounded at the corners of an octahedron by chlorine atoms, and every chlorine atom similarly by six sodium atoms. On the other hand Bragg[12] has shown conclusively that the single molecules of organic substances, and perhaps of some inorganic compounds, are retained intact in the lattice, and that the actual symmetry of single molecules is the determining factor of crystallographic symmetry. Thus a single completely asymmetrical molecule in a unit cell can produce only the asymmetrical triclinic system; the higher symmetry of the monoclinic and orthorhombic systems is attained by placing 2 or 4 or 8 whole asymmetrical molecules in the unit cell properly oriented about planes or centers of symmetry. As a sort of middle ground between the lattices of sodium chloride and of organic compounds, there may be cited the examples of the hexammoniates of the nickel halides[11] and the hexahydrate of zinc bromate.[13] In the single molecule of $Ni(NH_3)_6Cl_2$, six molecules of ammonia are bound to the nickel atom

by secondary valence forces, and the two chlorine atoms by primary valence bonds. In the crystal lattice each nickel atom is still surrounded symmetrically by six ammonia molecules, but there are not two but *eight* equidistant chlorine atoms in the same way that there are six chlorine atoms around each sodium atom in sodium chloride. The compound $Zn(H_2O)_6$-BrO_3 is exactly analogous.

It cannot be denied that the forces which hold organic molecules fixed in crystal lattices, or which enable very long molecules lying parallel to form liquid crystals, or which cause the molecules of almost all organic substances to become very definitely oriented in surfaces, are the same kind of forces which hold electrically neutral molecules of ammonia or water to metal atoms, either in the single molecule or in the crystal lattice. Now it has been proven that precisely the same thing is true of the halogen groups in polyhalides, even though the forces are holding together three atoms, or even more, of the same chemical nature, instead of grouping neutral atoms or molecules around a central atom of greatly different nature.

If planes are drawn through the lattices of the four experimentally studied trihalides so as to enclose $^1/_2$ instead of one molecule, then the metal atoms and the heaviest (previously body-centered) halogen atoms appear alternately at the corners of the new unit, while one atom of iodine in KI_3 or CsI_3, one atom of bromine in $CsIBr_2$, or one atom of chlorine in $CsICl_2$ lies on the body diagonal at .46 or .50 or .38 of its length from a corner iodine atom. Hence the structures are remarkably closely related to the simple halide unit cubes. A halogen atom in the latter case is replaced by a polyhalide group. Dimensions are changed and perfect cubic symmetry destroyed, but every metal atom is surrounded by six complex halogen groups, each acting as a single point in the lattice. The single primary valence bond of the chemical molecule is split in the lattice, but the secondary valence group within itself is retained intact.

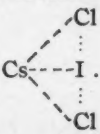
It has already been stated that the stability of the alkali polyhalides depends upon the metal—as a matter of fact relative stabilities are directly proportional to the atomic volumes of the metals. This is now easily explained. The size of the metal atom in the lattice determines the dimensions of the unit cell, or the interplanar distances, other things being equal. The smaller the dimensions the more difficult it is for three halogen atoms to lie on a straight line within the cell with any degree of stability. Halides of potassium are just able to form polyhalides; as a matter of fact only the iodide is able to form such compounds sufficiently stable to isolate. The size of the potassium atoms and the interplanar distances are such that upon the formation of KI_3 the string of iodine atoms predominates, the frame-work of the potassium atoms is distorted unequally in different directions, and the resultant properties approximate those of elementary iodine crystals. The compound NaI_3 does not exist because, even if the

I_3 groups were compressed in the lattice, the attraction of two iodine atoms under these circumstances far outweighs the ability of the sodium atom to hold three iodine atoms in spatial distribution. The equilibrium expression $I^- + I_2 \rightleftarrows I.I_2^-$ holds just as truly in the formation of solid crystal lattices as it does in ionized solution. Hence even in the very stable CsI_3 the reaction is easily sent from right to left by the application of mechanical compression or by increasing kinetic energies of vibration by means of heat.

The newly determined crystal structures of the trihalides present interesting evidence bearing upon the general question of the additivity of atomic radii. In the case of CsI_3, for example, the diagonal along which lie 1 atom of cesium and 3 atoms of iodine has a length of 10.6×10^{-8} cm. This is appreciably smaller than the sum of 1 cesium diameter plus 3 iodine diameters as evaluated under different assumptions by Bragg, Richards, Davey and others.[14] Hence the I_3 group must be very considerably compressed so that the atoms may be pictured as flattened in the direction parallel to the crystal cell diagonal into a shape something like that of red blood corpuscles. The experimental results are further proof of the validity of the conception of compressible atoms so long advanced by Professor T. W. Richards and of the incorrectness of the hypothesis of constant atomic radii.[15]

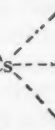
It is interesting to note that it is possible to prepare CsI_5. Wells and Penfield[4] claim that the crystals are triclinic. If this is true it may be safely predicted upon the basis of the present analyses, that the lines joining the two iodine atoms on each side of the center to the central iodine atom *will intersect at an angle.*

Finally, it may be asked whether any formula can express the constitution of the alkali polyhalides. It is obvious that none can express all the facts. The X-ray data gives the only absolute picture of the constitution of the solid state. The nearest approach to a mechanical formulation would express the empirical formula $CsICl_2$ as

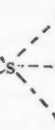


. The dotted lines mean not an increase in the number of primary valences for cesium, but a split one. The expression shows the halogens bound together by secondary valences, with the heaviest halogen at the center, so that a singly acting unit is produced; and yet each single halogen atom also comes under the direct influence of the metal atom. Otherwise it would be difficult to explain the mechanism whereby $CsICl_2$, prepared by passing chlorine into a solution of CsI, should decompose into CsCl and ICl. It is of course perfectly natural that the strongest halogen should remain bound to the

metal. Furthermore, by a simple consideration of balance the formula



shows why should be, and is, more stable even than



Even with these advantages, however, the formula falls far short of expressing correctly all the facts which crystal structure determinations have revealed.

[1] NATIONAL RESEARCH FELLOW.

[2] Clark and Duane, these PROCEEDINGS, **8**, 90 (1922); *Ibid.*, April, 1923.

[3] Wells and Wheeler, *Zs. anorg. Chem.*, **1**, 442 (1892).

[4] Wells and Penfield, *Amer. J. Sci.*, **43**, 21, 475 (1892).

[5] Ephraim, *Ber. deut. chem. Ges.*, **50**, 1069 (1917).

[6] Remsen, *Amer. Chem. J.*, **11**, 291.

[7] McCombe and Reade, *J. Chem. Soc.* (London), **123**, 141 (Feb., 1923).

[8] Küster, *Zs. anorg. Chem.*, **43**, 53 (1905); **44**, 431 (1905); **46**, 113 (1905).

[9] Kraus, *J. Amer. Chem. Soc.*, **44**, 1216 (1922).

[10] Wyckoff, *Ibid.*, **42**, 1100 (1920).

[11] Wyckoff, *Ibid.*, **44**, 1239, 1260 (1922).

[12] Bragg, *J. Chem. Soc.* (London), **121**, 2766 (Dec., 1922).

[13] Wyckoff, *Amer. J. Sci.*, **4**, 188 (1922).

[14] Clark, *Science*, **55**, 401 (1922).

[15] Cf. also Wyckoff, these PROCEEDINGS, **9**, 33 (Feb., 1923). The radius of the chlorine atom calculated from $CsICl_2$ is unusually small as it should be since it is measured along the diagonal in the direction of greatest compressing forces. For this reason the direct application of this dimension to other chlorine compounds has little meaning.

THE CRITICAL AND DISSOCIATION POTENTIALS OF HYDROGEN

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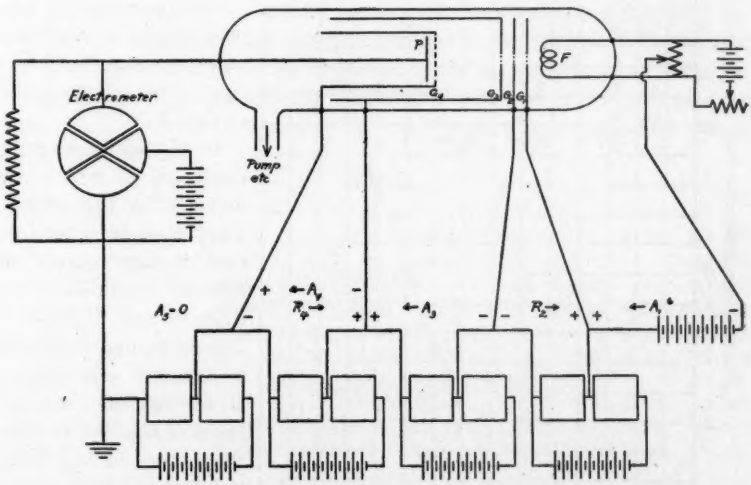
When electrons collide with gas molecules the collisions are elastic, or nearly so, until the electrons acquire a definite velocity. This velocity is characteristic of the gas. The potential through which the electrons must fall to attain this velocity is called a critical potential. The determination of the critical potentials of hydrogen has been the object of many investigations during the last ten years, but considerable uncertainty still attaches to their exactness. Thus the potential ascribed to the dissociation of the hydrogen molecule and the ionization of one of the resultant atoms was found by Franck, Knipping and Krueger[1] to be 17.1 volts, whereas Boucher[2] reports 15.6 volts for the same phenomenon. Recently

Franck[3] has reduced his value by 0.7 volt. It seemed desirable therefore to attempt a more accurate determination of this potential, for this method furnishes one of the best means of calculating the heat of dissociation of hydrogen.

Figure 1 shows the details of the vacuum tube used in this experiment, and also a diagrammatic representation of the electric fields. F is a platinum filament covered with calcium oxide. The two metal discs, G_1 and G_2, have slits 4 mm. long and 1 mm. wide at their centers. The nearer end of the cylinder G_3 is fitted with a similar slit, and all are so placed that they are in alignment with the hottest portion of the filament. The receiving end of the ionization cylinder consists of a plate, P, and gauze, G_4,

Fig: 1



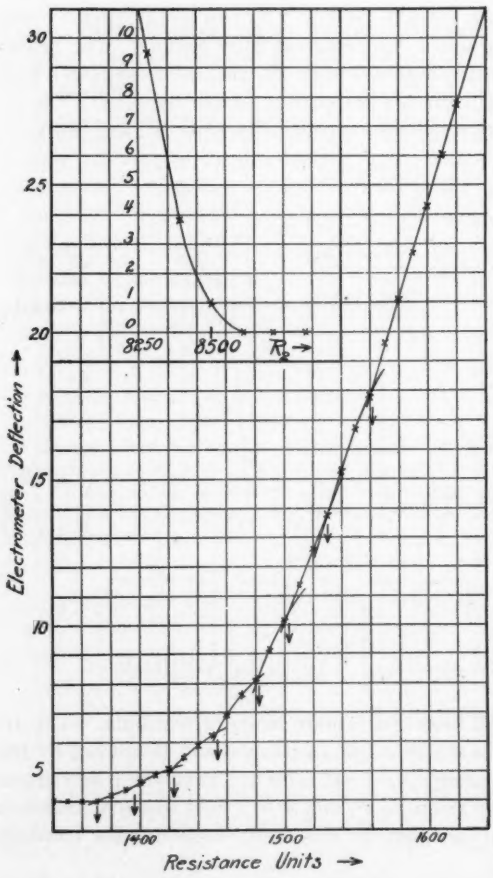
about 3 mm. distant. All metal parts were made of platinum. The arrows show the direction in which a free electron would be moved by the fields. In the following paragraphs A will refer to a field which accelerates an electron moving toward the plate P, and R to a field which retards such an electron. A quadrant electrometer was used, employing the constant deflection method.

The hydrogen was generated by electrolysis of barium hydroxide solution, passed over hot platinized asbestos, and stored over phosphorus pentoxide. During the experiments the pressure of hydrogen in the tube was about 0.1 mm. of mercury.

The initial electron velocity was determined by a method described by Horton and Davies.[4] Field A_1 was fixed at 18.0 volts, R_2 at 21.53 volts, A_2

at 2.0 volts, and A_4 at 27.0 volts. R_2 was first reduced until the electrometer showed a large deflection, and then increased until the deflection was again zero. From the value of R_2, at which the deflection is just noticeable, the initial velocity can be calculated. During a run R_2 was set somewhat lower than this extinction point in order to obtain a larger current; the amount of the lowering was varied from run to run, so as to eliminate accidental breaks in the current voltage curves. Field A_4 was reversed to R_4 of 27 volts, A_3 was increased by approximately one-tenth volt steps, and the deflection of the electrometer recorded.

Fig. 2



In all eight runs were made, all of which are included in this article. They resemble the current voltage curves of mercury published by Franck and Einsporn.[5] The particular run shown in figure 2 was chosen as an example, not because it was better than the others in any way, but because each observation was checked by three independent observers. All readings of the acceleration potential were taken in resistance units, and plotted against the electrometer deflection. The breaks in the curves were read off, converted into volts, and the initial correction added. The absolute values of these points therefore were not known until the final calculation was made. This rather roundabout procedure was adopted to avoid being influenced by known theoretical values. In most cases independent graphs were made by both

authors. The breaks thus obtained checked within a few hundredths of a volt. Table I gives a summary of all the breaks.

TABLE 1

RUN	INITIAL CORRECTION								
1	2.29	15.30	15.86	16.02	16.40	16.70			
2	3.18	14.75	15.09	15.34	15.79	16.19	16.68		
3	.75	14.89	15.09	15.44	15.74	16.14	16.34	16.71	
4	1.39	15.25	15.61	15.92	16.16	16.33	16.68		
5	1.24	14.75	14.97	15.29	15.56	15.85	16.05	16.32	16.63
6	1.28	15.17	15.41	15.70	15.89	16.14	16.36	16.56	16.73
7	1.61	14.94	15.33	15.54	15.78	16.10	16.35	16.70	
8	2.08	14.89	15.08	15.28	15.56	15.76	16.38	16.62	

If we assume that the highest break recorded corresponds to the voltage required to dissociate the molecule and at the same time to ionize one of the resultant atoms, we obtain a value for the dissociation potential for each run by subtracting the voltage corresponding to the head of the Lyman series (13.52). These values are found in the second column of table II. Furthermore, if we subtract the dissociation voltage found in this manner from each of the breaks recorded in table I we obtain the other values given in table II.

TABLE 2

RUN	DISSOCIATION									
1	3.18		12.12			12.68	12.84		13.22	(13.52)
2	3.16	11.59	11.93			12.63	13.03			(13.52)
3	3.19	11.70	11.90	12.25	12.55		12.95	13.15		(13.52)
4	3.16		12.09		12.45	12.76	13.00	13.17		(13.52)
5	3.11	11.64	11.86	12.18	12.45	12.74	12.94		13.21	(13.52)
6	3.21		11.96	12.20	12.49	12.68	12.93	13.15	13.35	(13.52)
7	3.18	11.76		12.15	12.36	12.60	12.92	13.17		(13.52)
8	3.10	11.79	11.98	12.18	12.46	12.66			13.28	(13.52)
Av.	3.16	11.70	11.98	12.19	12.46	12.68	12.95	13.16	13.27	(13.52)
Lyman			12.02			12.68	12.98	13.14	13.24	13.52

On comparing these values with the Lyman series, it will be seen that five of these breaks, in addition to the ionizing potential, apparently correspond very closely to this series. We can therefore obtain a value of the dissociation potential for each value of the Lyman series by subtracting the theoretical value from the corresponding observed value of table I. The average dissociation potential thus obtained is 3.15 volts, which checks the value given in table II. The average deviation of the average values from the theoretical values is only two-hundredths of a volt. For some unexplained reason the first term of the series does not appear in any run. The other three breaks may be critical potentials of the molecule, and therefore the dissociation potential should be added to the values for these points given in table II.

Summary.—The dissociation potential of the hydrogen molecule is

found to be 3.16 volts. Eight breaks in the current-potential curves are recorded, five of which are identified with the Lyman series, the remaining three being ascribed to the hydrogen molecule.

This work was begun while the first author was a National Research Fellow in Chemistry. He takes this opportunity of expressing his thanks to the National Research Council.

[1] Frank, Knipping and Krueger, *Verhand. deut. physik. Ges.*, **21**, 728 (1919).
[2] Boucher, P. E., *Physic. Rev.*, **19**, 189 (1922).
[3] Franck, J., *Zs. Physik.*, **11**, 155 (1922).
[4] Horton and Davies, *Proc. Roy. Soc. London*, **A98**, 134 (1920).
[5] Franck and Einsporn, *Zs. Physik.*, **2**, 18 (1920).

THE REFLECTION BY A CRYSTAL OF X-RAYS CHARACTERISTIC OF CHEMICAL ELEMENTS IN IT

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Communicated, February 14, 1923

Since our announcement in a former note[2] of a new method of crystal analysis by X-rays we have made further experiments which have enabled us to detect and study separately the reflections of rays belonging to the characteristic line spectra of the different chemical elements in the reflecting crystal. In the crystals thus far investigated—KI, KI_3, CsI, CsI_3 and $CsIBr_2$—X-rays characteristic of cesium, iodine and bromine have been identified. These rays, produced by the excitation of atoms in crystals, obey the law $n\lambda = 2d \sin \theta$. They are in addition to and entirely different from the anomalously reflected characteristic X-rays of iodine from KI, reported in another note. Inasmuch as the general phenomenon has not been discovered heretofore, it is the purpose of this note to present a brief summary of the experimental results bearing upon this kind of characteristic reflection.

In the first procedure in the analysis of crystals (l. c.) the ionization chamber is fixed at a convenient angle and the *general* radiation from a tungsten-target Coolidge tube allowed to impinge upon the crystal. By turning the crystal a series of peaks is produced, each one corresponding to reflection from a set of parallel planes in the crystal, such as those designated 100, 110, 120, 130, etc. For a cubic crystal, for instance KI, the 100 and 110 peaks are 45° apart, etc.

In the next step the wave-length corresponding to each peak is determined from the critical voltage and the quantum equation

$$Ve = hc/\lambda, \qquad (1)$$

and the perpendicular distance between the given set of planes from the equation

$$n\lambda = 2d \sin \theta. \qquad (2)$$

In the case of crystals in which a given set of parallel planes are all alike and equally spaced, the method of analysis just outlined usually suffices. For complex crystals, however, in which the planes may not be alike or equally spaced, the following extension often furnishes important data. This consists in determining the spectrum of the reflection from a set of planes by setting on the peak corresponding to that set, for example the 100 planes, and then changing by steps the angles of both the crystal and the ionization chamber, moving the latter at twice the rate of the former. Instead of finding a series of peaks corresponding to *different* sets of planes, the reflection from the 100 planes *alone* is analyzed.

The spectrum of the 100 planes of KI shows a series of well defined peaks[3] decreasing in intensity with increase in the angle, θ. These peaks appear always when the X-ray tube is operated at a potential above 33,000 volts. They cannot be due to reflection of the K-series line spectrum of the tungsten target, since a potential above 69,300 volts is required for its generation. The first peak, at an angle slightly greater than 3°, is characterized by a sharp absorption drop on the short wave-length (smaller angle) side, a peak at the top of this drop, and a smaller, symmetrical but incompletely separated peak on the long wave-length side. It was possible in our experiments to determine at once by the critical voltage method the wave-lengths corresponding to the center of the absorption drop, the higher and the lower peaks. The experiments gave the wave-lengths .374, .388 and .437 Å., respectively. These are the known values of the critical absorption, the K_β and the K_α wave-lengths of iodine. The smaller peaks at larger angles are the higher order reflections of the same characteristic radiations, facts which we checked both by the angle and by the critical voltage measurements of λ.

In more than 10 different determinations with different crystals of KI and using orders to the sixth, we have found the values of d to lie between 3.532 and 3.535×10^{-8} cm. A representative series of data is given in table 1.

In our former note[2] d_{100} for KI was determined at an angle of 5.51°. The critical voltage was 18,600 volts, corresponding to $\lambda = .6642$ Å. which is a wave-length in the continuous X-ray spectrum. The value of d calculated from this wave-length and this angle coincides with the value calculated from the characteristic line spectrum as in table 1.

A further interesting confirmation that the spectra are characteristic of iodine is obtained from an experiment which we made with the 110 planes and an operating potential of 90,000 volts. *Both* the regular reflection of the line spectrum of the tungsten in the target and that of the secondary

TABLE 1

ANALYSIS OF THE SPECTRUM OF THE 100 PLANES OF KI. (62,000 VOLTS APPLIED TO X-RAY TUBE)

	IONIZATION CHAMBER ANGLE READING	θ	CRITICAL VOLTAGE	λ (FROM CRITICAL VOLTAGE)	DESIGNATION	d × 10^8 CM.
	174°–35′	0°				
Right	168°–30′	3°–2.5′	33,000	.374 Å.	$I_{abs.}$ (1st)	3.532
	168°–15′	3°–10′	31,840	.388	I_β (1st)	
	167°–25′	3°–35′	28,400	.435	I_α (1st)	
	162°–25′	6°–5′	33,000	.374	$I_{abs.}$ (2nd)	3.532
	162°–0′	6°–18′	31,500	.391	I_β (2nd)	
	160°–20′	7°–7.5′	28,250	.437	I_α (2nd)	
	156°–21′	9°–7′	(Calcd. 9°–7.5′)		$I_{abs.}$ (3rd)	
	155°–30′	9°–32′	(Calcd. 9°–30′)		I_β (3rd)	
	153°– 5′	10°–45′	(Calcd. 10°–45′)		I_α (3rd)	
Left	180°–40′	3°– 2.5′	33,000	.374	$I_{abs.}$ (1st)	3.532
	180°–55′	3°–10′	31,840	.388	I_β (1st)	
	181°–40′	3°–32.5′	28,250	.437	I_α (1st)	

rays characteristic of iodine atoms in the crystal appeared. In our former note the value of d_{110} was found to be 2.495×10^{-8} cm. from the critical voltage, 26,310 volts, and the corresponding wave-length, $\lambda = .470$ Å., at the angle 5°–30′. Using this value of d the wave-lengths corresponding to each peak appearing in the spectrum were calculated. The remarkable concordance between these calculated wave-lengths and the known true values characteristic of tungsten and of iodine is illustrated in table 2.

TABLE 2

ANALYSIS OF THE SPECTRUM OF THE 110 PLANES OF KI. (90,000 VOLTS APPLIED TO X-RAY TUBE)

CRYSTAL TABLE ANGLE	θ	DESIGNATION	λ (CALCD. FROM $d = 2.495$)	λ (TRUE)
13°–37′	0°			
15°–45′	2°– 8′	W_β	.185 Å.	.1842
16°– 2′	2°–25′	W_α	.210	.211
17°–54′	4°–17′	$I_{abs.}$	.374	.3737
18°– 3′	4°–26′	I_β	.387	.388
18°–25′	4°–48′	W_α (2nd)	.210	
18°–40′	5°– 3′	I_α	.439	.437

In addition to the check in the value of d_{110} this spectrum shows (1) that the characteristic iodine reflections are more intense than the tungsten lines; and (2) that, whereas the α-peak is always higher than the β-peak for the regular reflected target line spectrum, the reverse is true for radiation characteristic of elements in the crystal. In all such cases so far investigated the α-peak is always *smaller* than the β.

With KI_3, the structure of which will be reported in detail elsewhere, exactly the same kind of characteristic iodine spectra have been obtained as for KI. The first order I_β and I_α peaks are at 2°–21′ and 2°–39′.

Calculating d from .388 = 2d sin (2°–21′) and .437 = 2d sin (2°–39′), the value 4.70×10^{-8} cm. is obtained. At $\theta = 6°–45'$ the critical voltage for the 100 peak is 11,300 corresponding to $\lambda = 1.09$ Å. and $d = 4.69 \times 10^{-8}$ cm. The crystal unit of KI_3 is a cube slightly distorted into a monoclinic prism, since the angle between the 100 and the 110 planes is 45°–12′. Wells and Penfield have observed from goniometric measurements a slight inclination of one axis to the plane of the other two. The unit contains $^1/_2$ molecule. Consequently the original unit cube of KI with $d = 3.532 \times 10^{-8}$ cm. has expanded to an edge length of 4.70×10^{-8} cm. with an extra atom of iodine at or near the center.

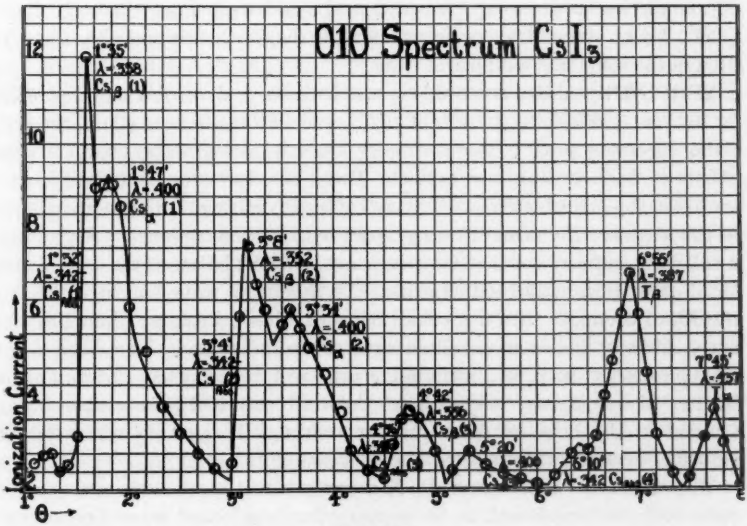

FIGURE 1

One of the most striking cases of characteristic emission from crystal atoms we have obtained with CsI_3, in which the parallel planes are not alike. Proceeding in the manner described for KI the spectrum for the 010 planes shown in the figure was obtained. Each peak and absorption drop has been labelled with the wave-length obtained by substituting in equation (1) the corresponding *measured* critical voltage. It is found that 4 orders of characteristic cesium peaks appear, and in addition the I_β and I_α peaks at 6°–55′ and 7°–45′. Thus it becomes possible to analyze separately the space distributions of both the cesium and the iodine atoms —and this in spite of the fact that cesium and iodine lie so close together in the table of chemical elements.

From the angles and wave-lengths substituted in equation (2) d_{010} for

cesium is 6.43×10^{-8} cm., and for iodine is 1.609×10^{-8} cm. Hence planes containing iodine atoms are $^1/_4$ as far apart as those containing cesium atoms. We find CsI_3 to be a rhombic crystal (the first of the type to be completely analyzed), for the parameters are different along different perpendicular axes. The spectra of the 100 and 001 planes, however, are like the spectrum of the 010 planes except that the peaks occur at different angles. For the 100 planes the first order Cs_β peak is at 2°–14′ and the I_β peak at 9°–59′. Hence d_{Cs} is 4.49 and d_I is 1.12×10^{-8} cm. For the 001 planes the first order Cs_β peak is at 1°–26′ and the I_β peak at 6°–21′, with corresponding values of d of 7.04 and 1.76×10^{-8} cm. The crystal unit therefore must be a rectangular parallelopiped with cesium atoms at each corner and iodine atoms at the center and equidistant along the body diagonal. From symmetry considerations the diagonals are probably distributed in the same way as those of FeS_2.[4]

With $CsIBr_2$, also a rhombic crystal with the values of d equal to 4.26×10^{-8} cm. (100), 5.91×10^{-8} cm. (010), and 6.90×10^{-8} cm. (001), the first order spectrum peak is more complex since it contains the characteristic effects of both cesium and iodine. These are, however, completely separated in the higher orders with remarkable distinctness. The iodine planes in this case are the same distance apart as the cesium planes. Singularly a tall peak appears for the 100 spectrum at 6°–28′, between the second and third order cesium and iodine peaks. If this has a wave-length of .929 Å., the K_β of bromine, then d_{Br} comes out such that a bromine plane lies exactly midway between a cesium and an iodine plane. The analysis of this crystal is, however, incomplete and will be reported in detail after further investigation. Crystals of CsIBrCl and $RbICl_2$ are also being studied in the hope of detecting the reflected X-rays characteristic of chlorine, as well as of the other heavier elements.

The reflection of characteristic X-rays described in this note seems to be reasonably well explained by the assumption (mentioned in our first paper) that a primary X-ray excites secondary characteristic X-rays in atoms with a certain time lag, approximately the same for all atoms of one kind. It is not necessary to assume that the primary ray has wave-lengths, but only that it must have been produced by a voltage above certain critical values. If the secondary rays have wave-lengths they will interfere and produce beams in the required directions. This point of view, however, does not appear to be compatible with the law of the conservation of energy applied to the processes going on in individual atoms.

[1] NATIONAL RESEARCH FELLOW.

[2] These PROCEEDINGS, 8, 90 (May, 1922).

[3] Curves illustrating this spectrum will be published shortly.

[4] Bragg, *X-Rays and Crystal Structure* (1916), p. 132.

ON THE ABNORMAL REFLECTION OF X-RAYS BY CRYSTALS

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Communicated, February 7, 1923

In the research described in this note we have examined in greater detail certain abnormal reflections of X-rays by crystals which we described (and which we called X-peak reflections) in a note communicated to the Academy on April 4, 1922, and printed in these PROCEEDINGS, May, 1922 (90–96).

We showed that under certain experimental conditions a crystal reflects rays that appear to have the wave-lengths characteristic of one of the chemical elements in the crystal itself. When one examines spectra by means of an X-ray spectrometer in the ordinary way the crystal reflects strongly rays belonging to the characteristic line spectrum of the target in the X-ray tube. In our experiments, however, the *abnormally* reflected rays appeared to have wave-lengths equal to those in the line spectrum of a chemical element in the crystal. We obtained evidence for these wave-lengths by determining the critical value of the voltage below which the reflections do not occur. In these experiments we used a crystal of potassium iodide and the critical voltage corresponded with the critical voltage for the K series of iodine. In certain experiments with photographic X-ray spectrometers, spots have been observed on photographic plates that did not correspond with normal reflections of the X-rays. No one has demonstrated experimentally, however, that the X-rays producing these spots had the wave-lengths corresponding to the line spectra of the chemical elements in the crystals. These photographic spots may, however, represent reflections of X-rays characteristic of chemical elements in a crystal, but they may, perhaps, correspond to certain reflections that we have observed but have not yet examined carefully. These reflections are represented by small peaks, some of which appear on the curves contained in fig. 1 (below). These small peaks correspond to reflections that are very much weaker than those that we are now discussing under the name of X-peak.

The X-peak reflection appears to be a very large phenomenon. Under certain experimental conditions it is stronger than the normal reflection from any of the principal planes of the crystal.

The normal reflection of X-rays by a crystal obeys the following two laws: firstly, the angle of incidence of the rays on a set of planes in the crystal equals the angle of reflection from these planes, and secondly, the equation

$$n\lambda = 2d \sin\theta \qquad (1)$$

gives the wave-lengths, λ, in terms of the angle of incidence, θ, and the distance between the planes, d. We have been able to show experimentally

that the abnormal reflection of rays characteristic of a chemical element in the crystal does not obey either of these laws.

By setting the ionization chamber of the spectrometer in given positions and by turning the crystal until the abnormally reflected ray entered the chamber, we found that there is no plane fixed in the crystal that always makes equal angles with the incident and reflected rays, no matter what the position of the chamber may be.

In the following discussion we will call the angle drawn to the centre of the slit of the ionization chamber, α. It equals the total deviation produced in the path of the rays by the crystal. We have determined the

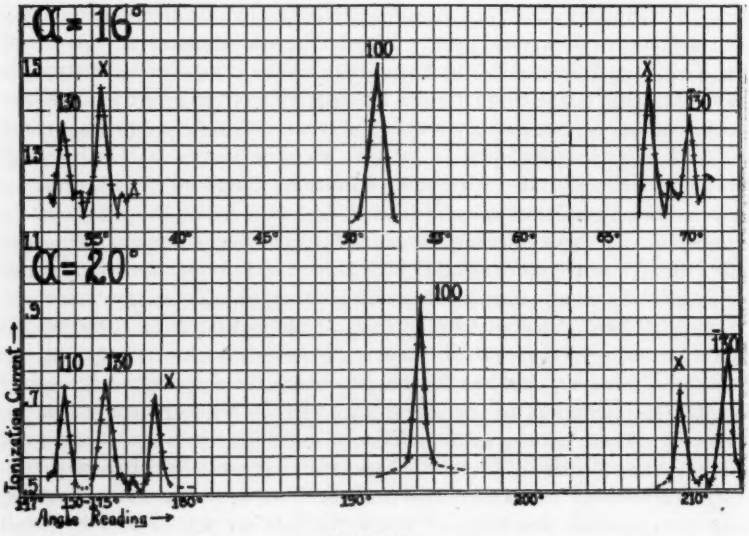

FIGURE 1

settings of the crystal required to reflect rays into the ionization chamber from the 100 planes, the 130 planes and the abnormal X-peak reflection for a number of values of the angle α. Fig. 1 represents the data obtained for two of these series of measurements; namely, for those in which α equals 16° and 20°. The reflections due to the 100 planes, the 130 planes, etc., and the X-peak are marked on the curves. In the original experiments described in the previous note, α equaled 11° and the X-peak fell very close to the 130 peak. As α increases, however, the X-peak moves away from the 130 peak toward the 100 peak.

The curves in fig. 2 give the results of eighteen sets of experiments at different angles, α. It will be seen that in the case of reflection by the 100 planes or by the 130 planes, the position that the crystal must occupy in

order to reflect rays into the ionization chamber changes half as fast as the position of the ionization chamber changes. If α increases by a certain number of degrees the crystal angle must be changed by half that number of degrees. In other words, the angle of incidence equals the angle of reflection, and each equals half the total angle of deviation of the rays. This, however, is not true of the X-peak.

For small angles, α, the X-peak lies outside of that due to reflection from the 130 planes. For larger angles, α, the X-peak lies between those due to reflection from the 100 and 130 planes. Further, there are always two X-peaks, on the two sides respectively of the peak representing reflection from the 100 planes and at equal angles from it. The same is true for the 010 planes and the 001 planes.

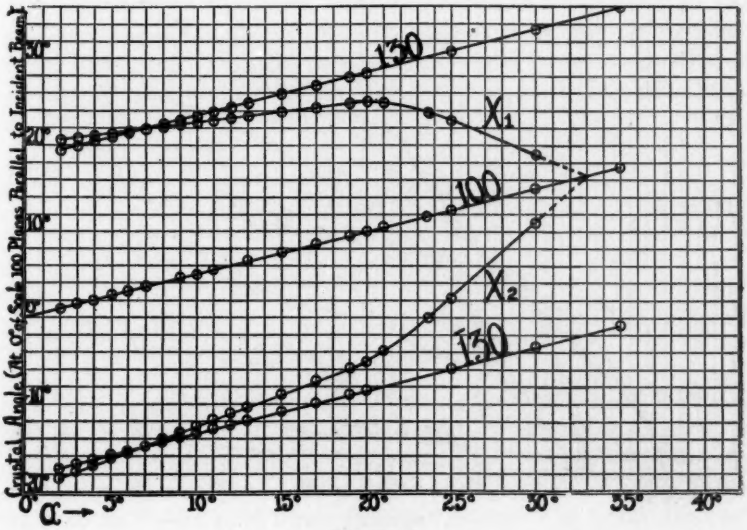

FIGURE 2

At an angle, α, equal to about 23°–40′ the X-peak appears when the crystal angle is 0; i.e., when the 100 planes lie parallel to the incident beam. This has been verified both by ionization spectrometer measurements and by Laue photographs which will be reproduced in a later paper. Corresponding to this, there is an X-peak for the same angle, α, when the crystal angle is 23°–40′, which means that in this case the 100 planes lie parallel to the reflected ray.

That the wave-lengths of the X-rays reflected in the X-peaks do not obey the law expressed by equation (1) may be inferred from the following experimental results: by setting on the X-peaks at various angles, α, and

by reducing the voltages applied to the X-ray tube we have determined in each case the critical voltage required to produce the reflection. This voltage substituted in the quantum equation

$$Ve = h\nu = hc/\lambda \qquad (2)$$

gives us the wave-length of the reflected beam of rays.

The curves in fig. 3 represent the data for nine values of the angle, α. It appears that in each case the ionization current vanishes when the voltage applied to the tube is about 31.5 kilovolts. Substituting this in equation (2) we get $\lambda = .392$, which is a wave-length lying between the α and the β lines in the K series of iodine (namely $\lambda_\alpha = .437$ and $\lambda_\beta = .388$). It follows from these observations that the wave-lengths reflected in the

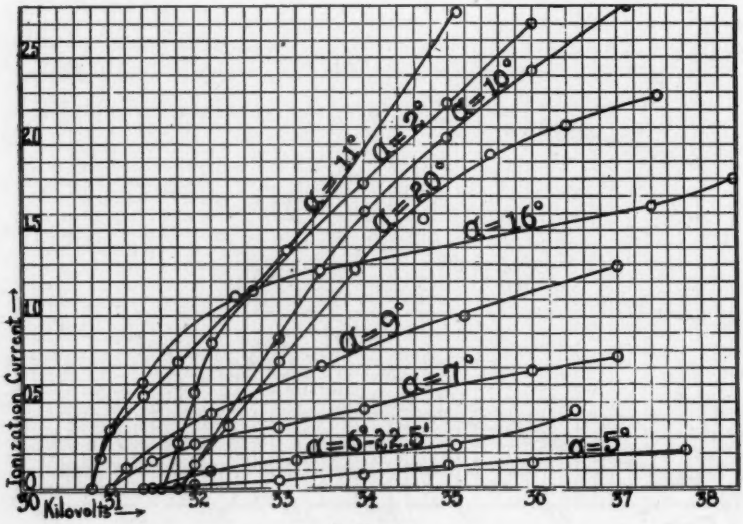

FIGURE 3

X-peaks are equal to each other, within the limits of error of the measurements, for all the total angles of deviation α and, therefore, that this characteristic reflection does not obey equation (1).

From our voltage measurements we infer that the crystal does not produce the X-peak reflection unless the incident beam contains X-rays of shorter wave-lengths than those in the K series of iodine. A sheet of copper placed in the path of the reflected beam reduces the ionization current in the spectrometer much more markedly than, if the copper is placed in the path of the incident beam. This furnishes additional evidence that the reflected rays have longer waves than the incident rays which produced them have.

The X-peak reflection is not a phenomenon peculiar to the particular crystal of potassium iodide employed in the experiments. We have used four different crystals of potassium iodide with the same results in each case.

No adequate explanation has, as yet, been found for this peculiar reflection in the X-peak.

McKeehan has published a theory of what he calls "Extraordinary Diffraction of X-rays" and he suggests that his theory may explain the X-peak reflection. His equations, however, contain the wave-lengths of the incident beam of rays whereas the position of the X-peak in our experiments does not appear to depend upon the voltage applied to the X-ray tube; that is, does not depend uyon the wave-lengths of the incident rays, provided only that they are shorter than the critical absorption wave-length of iodine. Further, McKeehan's equations do not give the observed angles at which the characteristic rays are reflected.

Perhaps a way of looking at the phenomenon more consistent with modern conceptions of the mechanism of radiation may be found in the points of view we suggested in our original note.

ELECTRIC CONDUCTION: HALL'S THEORY AND PERKINS' PHENOMENON

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Communicated, January 9, 1923

1. The free electron theory of electric conduction developed by Drude and others and discussed at great length in standard treatises by Richardson[1] and Jeans[2] had in its early days much success but today encounters many objections. For example, Jeans points out that the optical phenomena require a far higher degree of ionization in metals than can be reconciled with the specific heats; and on the other hand a low degree of ionization requires a longer free path than seems possible. He suggests the necessity of quantum theory in the premises. For several years, however, Hall[3] has been developing a dual theory of electric conduction where the ions play the preponderant rôle by favoring the advance of the state of ionization and the free electrons contribute comparatively little to the conductivity. According to this theory there need be no insuperable difficulty with the specific heats; but some other explanation than Schuster's[4] and Nicholson's[5] would have to be given for the optical phenomena. We are, however, by this time accustomed to the apparent necessity of dealing in quanta where radiation is concerned, and this need

no longer seriously disturb us. But even today we do not expect at room temperatures, to find great need of quanta in dealing with such phenomena as heat capacity and thermal or electric conduction.

2. There is one serious difficulty of a *statistical* nature in the free electron theory. The ordinary notion of the meaning of "free" in such a connection is that of a straight or nearly straight path between encounters. The notion comes from the theory of gases where it has done valiant service. Except through the intervention of the quantum theory or some such pervasive discontinuity with older ways of thought it is impossible to get any really "free" paths for electrons in metals. Consider for a moment an electron (movable) and an ion (fixed). The potential energy is e^2/r and the kinetic energy is $mv^2/2$. Unless $mv^2/2 > e^2/r$ the electron must describe an ellipse about the ion as focus and there will be in the sense of the gas theory nothing like a free path. This means $r > 2e^2/mv^2$. According to ordinary kinetic theory v is of the order of magnitude of 10^7 at room temperature, m is about 9×10^{-28}, e^2 is near 23×10^{-20}; and these data make $r > 5 \times 10^{-6}$. Hence unless an electron is removed by a hundred, or two, atomic diameters from an ion, there is no free path!

Physically this means that even if the un-ionized atoms are completely neutral electrically (outside of their sphere of action of diameter of the order of magnitude 3×10^{-8}) an ionization of as much as 1% would leave little or no opportunity for electronic free paths of the sort believed on rational grounds to exist in the case of gaseous molecules. Further it means that the general free-path arguments which are carried over from the kinetic theory of gases to the kinetic theory of conduction in metals (whether thermal or electric conduction) are transferred verbally and formally without much chance that the words mean at all the same sort of thing in the conduction problem as in the gas theory or that the symbols in the formulas can refer to things known to exist in the actual physical condition;—that there is no real logic in the transfer except as a posterori considerations may lead to an apt interpretation relative to the existing physical state.[6]

For example, the formula for the electric conductivity as often derived is

$$C = nLe^2V/6kT \quad \text{(Richardson, } loc.\ cit.\text{, p. 410)}$$

where n is the number of free electrons per cubic centimeter, L is the mean free path, $e = 4.774 \times 10^{-10}$ is the electronic change, V is the mean velocity of about 10^7 cm./sec. at room temperature, T is the absolute temperature, and k is the gas constant 1.37×10^{-16}. Now the conductivity C falls off with the temperature approximately as $1/T$ and V varies as $T^{1/2}$. Hence the product nL must vary approximately as $1/T^{1/2}$. So far as my reading goes, there is a good common-sense physical basis for the belief that the ionization resulting in the electron density n should increase

rather than decrease with the temperature. Such theory as there is appears to indicate also that the mean free path L, though not largely variable in gases with T, does tend to increase. Hence there would appear slight reason to believe that nL could fall off with increase of T. In such a theory as Bridgman's[6] the physical basis being different the conclusion might also be different.

With respect to the change of L with T, two points of view may be mentioned. Jeans[7] replaces the elastic spheres of diameter a by repulsive centres, which on the average will behave much like elastic spheres of some diameter a, but which permit a lengthening of L (effectively a decrease of a) with increasing temperature owing to the closer average approach of the centres when the average velocity of the molecules is greater. Sutherland,[8] however, considers the effect of an attractive force F acting between the spheres and shows that if a be the diameter of the elastic spheres the effective diameter so far as collisions are concerned becomes

$$a\left\{1+\frac{2}{3kT}\int_a^\infty F(r)\,dr\right\}^{1/2} \text{ and } L=\frac{1}{\sqrt{2}\,\pi a^2 n\left\{1+\frac{2}{3kT}\int_a^\infty F(r)dr\right\}}$$

Thus the postulation of an attractive force leads him to a result similar in sense to that reached by Jeans, viz., an increase of L with T. It is interesting to calculate the corrections to L necessary in the case of the electron if the ion be regarded as of diameter $a = 3 \times 10^{-8}$. We have[9]

$$L=\frac{1}{\pi\left(\frac{a}{2}\right)^2 n\left\{1+\frac{4e^2}{3kTa}\right\}}=\frac{1}{\pi\left(\frac{a}{2}\right)^2 n\left\{+1\frac{8\times 10^4}{T}\right\}}$$

This would show that the effect of attraction was the major determinant of L at all temperatures experimentally attainable.

Nobody would claim that Sutherland's calculation could apply in strictness to the case under discussion because of the interaction of electrons among themselves and of electrons and neutral atoms in addition to the action between electrons and ions; but it is worth while to bear in mind the very large effects on free paths of such large forces as act at a distance between charges. The free path should vary in this case almost directly as the temperature. Still a different slant on the problem may be had by considering the well-known formula for the electron density as a function of the potential. If there is anything approaching a thermal statistical equilibrium n should vary in the electrostatic field of the ion as $e^{-\phi/kT}$ where ϕ is the potential energy and is equal to $-e^2/r$. With rare ionization r might vary from about $a = 3 \times 10^{-8}$ to 10 or 100 or even 1000 times that amount. The value of ϕ/kT would be of the order $6 \times 10^4/T$ for $r = a$ (the distance of a diameter from the centre) and would decrease

to 1/10 or 1/100 or even 1/1000th of that amount. Thus the density of the electrons would vary greatly over ranges comparable to the ordinarily assumed free-path.

3. The theory of dual electric conduction due to Hall[3] avoids some of the physical difficulties of a pure electron theory. It has at least one fundamental physical advantage in that it takes account of the presence of the ions whose very existence has often been ignored, although from several points of view just mentioned it would seem as though the presence of the ions must very materially modify the whole statistical mechanics of the problem of conduction. How well time will serve Hall's theory one cannot forecast; but a recent discovery of Perkins[10] seems to fit well qualitatively with that theory. Perkins has shown that adding negative charge (electrons) to a conducting strip of graphite diminished the conductivity, which on the free electron theory must have been increased by the increase of n. He further showed that adding positive charge increased the conductivity, though presumably decreasing n. He thus asks: Il faudrait imaginer, pour rendre compte de ces faits, que la présence d'électrons de charge statique gêne le fonctionnement de la conduction, tandis qu'une électrisation positive le facilite? Moreover, he remarks that the effect is larger in magnitude than that which could be expected (of opposite sign) on the basis of a free electron theory of conduction with an ionization of one electron per atom. He finds the effect nil in gold.

Now although I hesitate, and take it for granted that Perkins himself hesitates, to place much reliance on the results of an experiment so delicate as his before it has been repeated on a variety of materials and analyzed critically with respect to every possible interpretation and experimental disturbance, this phenomenon of Perkins seems to me to be quite in line with the general point of view of Hall, and, as it is an effect of which I predicted the possibility in discussions of metallic conduction with my class in the constitution of matter last year, I may perhaps be pardoned for offering these considerations, somewhat tentatively, to a wider circle for criticism. One need not go into the various details of Hall's theory necessary to account for all the various effects he examines (Peltier, Thomson, Hall effects). The fundamental physical notion is that there is relatively low ionization and that the conductivity is mainly carried by the operation of the ions. It might be fair to assume that the conductivities C_a and C_f due to the ions and electrons are independent, additive, and proportional to the number of electrons (or ions) present (at least when that number is relatively small so that the actions of the different ions are fairly free from the influences of their neighbors). Then

$$C = C_a + C_f = An_a + Bn_f, \qquad n_a = n_f = N, \qquad A > B,$$

where n_a and n_f are the numbers of ions and of electrons (presumably equal in the neutral state), and where $A > B$ merely expresses the condi-

tion that the greater conduction is by the ions. If now a certain number of electrons (n per cubic centimeter) be added, so that the conductor is no longer neutral, it is possible and from the general point of view of equilibrium it is probable that some of the $n_f + n$ electrons are driven back into combination with the ions. Let ν (n) be that number.

Then after the applications of the negative charge the number of ions will be $n_a - \nu$ and of electrons $n_f + n - \nu$. The conductivity should be

$$C' = A(n_a - \nu) + B(n_f + n - \nu), \quad C' - C = -A\nu + B(n - \nu).$$

Now the number $\nu(n)$ recombining would be assumed to be an analytic function (we are not talking quanta, and might still have a practically analytic function even if we were). Clearly $\nu(0) = 0$ and, within the domain of linearity, we may write $\nu = \alpha n$ so that α is the fractional part of n which recombine. Then

$$C' - C = n[B - \alpha(A + B)], \qquad dC/C = [-\alpha + B/(A + B)]n/N.$$

The fraction $B/(A + B)$ on Hall's theory is small.[11] Consequently unless the fraction α is also small it would appear that there had been loss of conductivity by adding the negative charge and gain of conductivity by charging positively—as Perkins found. The values of α, A, B, N would differ from substance to substance and in the same substance with the temperature or other conditions. The relative effect is proportional to n/N, abstraction being made from the values of α, A, B. Hence for a given charge n the effect should be less in highly ionized substances (good conductors?) than in those of low intrinsic ionizations. This might easily explain Perkins' failure to find the effect in gold. It would be difficult to believe that in gold N is not very much larger than in graphite, possibly hundreds of times as large; there should not be anything like an ionization of one electron per atom in graphite.

Perkins writes and I have written as though a charge permeated a metal or other conducting strip whereas the charge is ordinarily supposed to reside on the surface of a conductor. Estimates have been made of the depth to which the charge descends[12] which would indicate in a general way that even in strips so thin as those used by Perkins the charge would be necessarily superficial. This need not invalidate the argument applied above. When dealing with a given piece of conductor the quantities n and N may equally well be the total number of added electrons and the total number of previously free electrons. If a negative charge is added, it may be imagined to neutralize the ions in the superficial layer so that the conduction tends to go more through the deeper body and less through the skin of the conductor; whereas if the charge is positive the relative density of ions in the skin is increased and the currents tend to go more in the skin and less in the depths of the conductor.[13] Perkins finds further that the decrease of conductivity due to a negative charge is 20% greater than the in-

crease due to an equal positive charge; but there are effects dependent on the square of the charge (superficial tension, for example) which would be the same for positive and negative charges of equal magnitude.

In the present unsatisfactory or unsettled state of our theories of electrical conduction in metals[14] and in the face of serious doubts not only with respect to the physical picture of the processes going on within a conducting metal[15] but even with respect to the applicability of statistical methods in cases where the mean free path is large compared with the uniformities of the electrostatic field, it is very hopeful to find a new, though difficult, method of experimental attack on the physics of metallic conduction; and that method should be pushed until it is thoroughly substantiated or overthrown, and if substantiated, it should be followed until a large amount of material has been assembled for theoretical codification.

[1] O. W. Richardson, *Electron Theory of Matter*, 2nd Ed., Chaps. 17 and 18.

[2] J. H. Jeans, *Electricity and Magnetism*, 4th Edition, especially pp. 306ff and 549ff.

[3] E. H. Hall, these PROCEEDINGS, **7**, March, 1921; **8**, October, 1922; **9**, February, 1923.

[4] A. Schuster, *London, Phil. Mag.*, **7**, February, 1904.

[5] J. W. Nicholson, *Ibid.*, **22**, August, 1911.

[6] P. W. Bridgman, *Ithaca, Physic. Rev.*, Ser. 2, **17**, 1921 (161–194) gives such an interpretation of these formulas on the basis of the physical state which he postulates for his "gap" theory of conduction. There are many points of similarity between the theories of Hall and Bridgman. If the atoms have the elongated Bohr orbits now assumed for the distribution of radial quanta, transfer of electrons at aphelia from neutral to neighboring charged atoms might seem highly probable.

[7] J. H. Jeans, *Dynamical Theory of Gases*, 1904, p. 254.

[8] Wm. Sutherland, writing from Australia, published a number of papers on kinetic theory which are approvingly cited by O. E. Meyers in his *Kinetic Theory of Gases* (English by Baynes) and which seem to contain some points of view not yet certainly to be ignored even though the details might no longer be approved. Particular reference may be made to Sutherland's paper in *London Phil. Mag.*, **36**, 1893 (507).

[9] In the case of an electron of vanishingly small radius compared with that of the ion, the radius of the ion replaces the diameter. Moreover when one set of molecules is at rest the factor $\sqrt{2}$ (given by some as 4/3) disappears.

[10] H. A. Perkins, *Paris, C. R. Acad. Sci.*, **175**, 1922 (363) and *Paris, J. Physique*.

[11] What Hall writes as k_f/k, the ratio of the free electron conductivity to the total conductivity, is our $B/(A+B)$ and according to him is assumed to be a quadratic function of the ordinary centigrade temperature, $k_f/k = C + C_1t + C_2t^2$. The variation with t is not very fast and the value at $t = 0$ is C which for the 17 metals tabulated (these PROCEEDINGS, March, 1921, p. 101) varies from 0.02 to 0.19.

[12] L. Silberstein, *London, Phil. Mag.*, **36**, 1918 (413).

[13] If one could assume that the charge penetrated the metal and could further assume as one may for gases (see Noyes and Wilson, these PROCEEDINGS, October, 1922, p. 203) that the law of mass action can be applied to the equilibrium between electrons and ions and neutral molecules, a probable value for α would be 1/2.

[14] H. A. Lorentz, *Theory of Electrons*, 2nd Edition, 1916, p. 67.

[15] See the conclusion (p. 878) of the long report of R. Seeliger, "Electronentheorie der Metalle," *Encyklopädie der Math. Wiss.*, Vol. V_2, Pt. 5, pp. 777–878, April, 1922. What I have tried to do is to use a minimum amount of detail in the physical picture.